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*S. W. Fowler, T. F. Hamilton, M. Coquery, J.- P.
Villeneuve, M. Horvat*

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CONCENTRATION OF SELECTED TRACE ELEMENTS AND PCBs IN SEDIMENTS FROM THE ADRIATIC SEA

Fowler S.W.¹, T.F. Hamilton^{1,2}, M. Coquery¹, J.-P. Villeneuve¹ and M. Horvat¹

¹*Marine Environment Laboratory, IAEA, Principality of Monaco*

²*Present address: HEAD, Lawrence Livermore National Laboratory, Livermore, USA*

Abstract

A broad baseline study of the levels and distributions of trace metals and PCB compounds in sediments has been undertaken. PCB concentrations in surface sediments reflect the source of these contaminants in the region. The highest PCB concentrations as Aroclor 1260 (approximately 10 ng g⁻¹) were found in sediments near the outflow of the Po river. The lowest concentrations (1.5 ng g⁻¹ dry) were associated with the sediments from the Jabuka Pit in the Middle Adriatic. These values are quite similar to total PCBs (<1.0-17) measured in surface sediments sampled off the coast of Croatia in 1977-78. Thus, based on the limited amount of new data available, it appears that there has been little, if any, decrease in PCB loading in Adriatic sediments over the past 15 years. Downcore profiles of PCBs in sediment cores are also discussed from a pollution history standpoint. Likewise, total mercury in surface sediments was also highest at stations off the Po (403-499 ng g⁻¹ dry) and lowest (67-224 ng g⁻¹) in the Jabuka Pit. In one core located just south of the Po outflow, total Hg concentrations at all depths were relatively high decreasing gradually from approximately 400 ng g⁻¹ in the top 4 cm to roughly 200 ng g⁻¹ at a depth of 32 cm. Using a ²¹⁰Pb-derived sedimentation rate of 0.26 cm y⁻¹ for this station, it appears that anthropogenic inputs of mercury may have been responsible for the gradual increase in total mercury noted over the last 125 years.

Key words: Adriatic, sediments, trace chemistry

1. Introduction

Several surveys of metal and organic pollution have been carried out in the Adriatic Sea over the last two decades. Most of these studies have been local in nature and focused in the northern sector (e.g., bays, lagoons, nearshore areas, Po outfall), and only few could be considered synoptic in their coverage (see UNEP 1989, 1990; Fowler 1987, 1990; Bernhard, 1988 for reviews). The ELNA project offered an excellent opportunity to obtain a series of surface sediment samples over a relatively wide area in the Northern and Middle Adriatic. In addition, to examine the historical record of anthropogenic pollution, cores were raised from nearshore and offshore areas to try and assess both spatial and temporal trends of such potentially important contaminants as PCB compounds, total Hg, methyl Hg, Ni, Co, Zn, Cr, As and Pb. Other sediment parameters such as carbon content and grain size have been used to aid in the interpretation of the pollutant data.

2. Materials and methods

During 1993-94, sediments were sampled with box corers from which subcores were taken on deck using 10-cm diameter PVC coring tubes. The length of the subcores averaged about 35 cm. The cores were immediately sectioned at depths of every one or two centimeters and the samples held either frozen or refrigerated until prepared for analysis in the laboratory. In all stages of sample collection, storage and preparation, extreme care was taken to avoid inadvertant contamination by metals and PCB compounds.

Water content of each sediment sample was determined by weight loss after freeze-drying. The dried solids were then ground into a fine powder using a mortar and pestle and stored in a dessicator.

The in situ bulk sediment densities were estimated using the water content and a mean particle dry density (ρ) of 2.56 g cm^{-3} . Sedimentation rates were derived using the ^{210}Pb technique, the details of which are given in Hamilton *et al.* (this volume).

Preliminary measurements of sediment particle size were conducted using a simple sieving and particle settling technique. Forty grams of sediment were first wet-sieved through 1 mm and $63 \mu\text{m}$ meshes. The remaining fraction was dispersed in a 1-litre graduated cylinder and at pre-determined times, 20 ml sub-samples were pipetted from specific depths in the cylinder and transferred to pre-weighed beakers. These sub-samples were then oven-dried, weighed, and the size fractions computed using standard Stokes' Law equations. This method was subsequently replaced by a laser granulometric technique which was used to measure selected horizons from a series of 10 sediment cores collected during the two summer cruises (ELNA 3 and ELNA 6). A 1-g homogenised sample from each horizon was diluted with distilled water and an aliquot transferred to the sampling unit of a Mastersizer Micro Laser Particle Size Analyser (Malvern Instruments). The Mastersizer uses both Mie and Fraunhofer diffraction theory to calculate the intensity of scattered light generated from a 2-mW Helium-Neon optical unit. The system is factory calibrated for sediment particles using NIST 1004B Standard Reference Sediment.

PCB methodologies. Three grams of each sample was added to a pre-cleaned extraction thimble in a soxhlet apparatus. PCB congener 29 (1 ml of $25 \text{ pg}/\mu\text{l}$) and epsilon HCH (1 ml of $20 \text{ pg}/\mu\text{l}$) were added as internal standards. Extraction was then performed with 200 ml of hexane for eight hours (with the cycling rate adjusted to 4 - 5 cycles per hour). Extracts were concentrated with a rotary evaporator to approximately 15 ml, dried with anhydrous sodium sulphate and then transferred to a Kuderna-Danish concentrator. The extract was then concentrated to 1 ml with a flow of nitrogen. Hexane Extractable Organic Matter (HEOM) was determined by evaporating measured, small volume (1 to $10 \mu\text{l}$) replicates ($n = 5$) of the extract on the pan of an electrobalance. Each extract was passed through a Florisil® (17 g) column which had been activated for eight hours in an oven at 130°C and partially deactivated with water (0.5% wt./wt.). From this column three fractions were collected. The first (F1) was eluted with hexane (70 ml), the second (F2) with hexane/dichloromethane (70:30 v/v, 50 ml) and the third with dichloromethane (40 ml).

Organochlorine compounds in fractions F1 and F2 were analysed using a Hewlett Packard 5880 gas chromatograph with split-splitless injection (250°C) and equipped with the appropriate standard H.P. ECD (maintained at 300°C). This instrument was fitted with an SE54 fused silica capillary column (25 m x 0.2 mm i.d.; $0.33 \mu\text{m}$ film thickness - H.P. Ultra series). The carrier gas was nitrogen ($1.5 \text{ ml}/\text{min.}$) and the oven temperature Program was 70°C for 2 min., 70 to 260°C at $3^\circ\text{C}/\text{min.}$ and 260°C isothermal for 20 min. Fractions were subsequently re-analysed using a higher resolution system. This comprised a Hewlett Packard 5890 Series II GC with split/splitless injection (250°C) and fitted with a G1123A H.P. electron capture detector (maintained at 300°C). Separations were performed using an SE54 fused silica column (50 m x 0.2 mm i.d.; $0.33 \mu\text{m}$ film thickness - H.P. Ultra series) with nitrogen carrier gas ($0.8 \text{ ml}/\text{min.}$) and temperature Programd as follows: 70°C for 2 min.; 70 to 280°C at $3^\circ\text{C}/\text{min.}$; isothermal at 280°C for 30 min. Better resolution to separate o,p'-DDT and cis-nonachlor was achieved using this second system. The F3 fractions were archived for future analyses.

Compounds were identified by comparison of retention times of peaks in sample extracts with those of authentic standards. Compounds typically quantified are listed below according to the fraction in which they elute from the clean-up technique:

<u>Fraction 1</u>	<u>Fraction 2</u>	<u>Fraction 3</u>
HCB	α HCH	dieldrin
p,p'-DDE	β HCH	endrin
o,p'-DDE	lindane	heptachlor epoxide
heptachlor	p,p'-DDT	methoxychlor
aldrin	o,p'-DDT	(this fraction was archived)
trans nonachlor	p,p'-DDD	

<u>Fraction 1</u>	<u>Fraction 2</u>	<u>Fraction 3</u>
PCB 8; PCB 18	o,p'DDD	
PCB 28; PCB 31	cis chlordane	
PCB 44; PCB 49	trans chlordane	
PCB 52; PCB 66	cis nonachlor	
PCB 87; PCB 101	+ internal standard: epsilon HCH	
PCB 105; PCB 110		
PCB 118; PCB 128		
PCB 138; PCB 149		
PCB 153; PCB 156		
PCB 170; PCB 180		
PCB 187		

+ internal standard: PCB 29

Sample extracts were diluted to bring peaks for quantification into the calibrated linear ranges of the instruments. Peak responses in the extract chromatograms were then compared with those of injected standards. From the volumes injected and the dilution of the extracts, concentrations were then calculated and further corrected for recovery (as determined from the recovery of the internal standards) and for any contributions from reagents (as shown by 'blank' analyses). Recoveries and separation efficiencies using the Florisil columns were routinely evaluated and chromatograms were checked for compounds usually associated with other fractions.

Mercury measurements. Total mercury was determined by digesting approximately 0.1 to 0.25 g of freeze-dried sediment with 4 ml HNO₃ (Merck, Selectipur, 70%) and 0.5 ml of HCl (Merck, Suprapur, 36%) in closed Teflon vials (25 ml, Savillex Corp., USA) at 90°C for 6 to 12 hours. Before the samples were diluted to the final volume (50 ml) with deionized water (MilliQ), 1 ml of BrCl oxidation solution was added. An aliquot of the sample was then passed through the SnCl₂ reduction, aeration, and amalgamation processes. Finally, mercury was detected by cold vapour atomic fluorescence spectrophotometry (CV AFS), a single amalgamation technique coupled with a Brooks Rand Ltd. AFS detector. Specific details of the method are given in Liang and Bloom (1993).

The methyl mercury method consisted of distillation, followed by aqueous phase ethylation, room temperature precollection on Tenax, and separation of ethylated mercury species on the GC column (a glass column, I.D. 4 mm, 60 cm long, operated isothermally at 110°C, carrier gas: argon, 30 ml/min.). Separated mercury species were then transformed into elemental Hg by pyrolysis at 900°C and swept into a cold vapour atomic fluorescence detector (CV AFS). The method is schematically presented in Fig. 1 and described in detail in previous publications (Horvat *et al.*, 1993, 1994; Liang *et al.*, 1994).

For quantification purposes sediments were dried at 105°C for 24 hours and all results for total and methyl mercury are expressed on a dry weight basis. Three blanks were also run together with the samples. The detection limits expressed as three times the standard deviation of the procedural blank are as follows: MeHg: 0.01 µg/Kg; Total Hg: 0.05 µg/kg. The accuracy of the results for determination of both total and methyl mercury were checked by analysing the Certified Reference Material IAEA-356, Polluted Marine Sediment (Horvat *et al.*, 1994). Our analyses resulted in excellent agreement with the certified value.

Trace element analysis. Two ml aliquots of the sediment digests that were prepared previously during the work-up for natural radionuclide analyses were analysed as element scans by Inductively-Coupled Plasma-Mass Spectrometry (ICP-MS) (VG Elemental, Winsford, Cheshire, UK). General information on machine settings, blanks and quantification with standards has been given by Fowler *et al.* (1992).

3. Results and discussion

PCBs. The locations where sediments were sampled for contaminant analyses are shown in Fig. 2. At St. 33 off the Po delta, a 32-cm core was also analysed. The results for total PCBs and the individual PCB congeners in surface sediments are set out in Table 1. From the data set, total PCBs in surface sediments clearly reflect the main source of these contaminants in the region. The highest PCB concentrations quantified either as Aroclor 1260 ($\sim 10 \text{ ng g}^{-1}$ dry) or Aroclor 1254 ($5\text{--}7 \text{ ng g}^{-1}$ dry) were found in sediments from the Northern Adriatic affected by the outflow of the Po river. The lowest concentrations ($0.9\text{--}2.3 \text{ ng g}^{-1}$) were associated with sediments from the Jabuka Pit in the Middle Adriatic.

In the Northern and Middle Adriatic, our values ($\sim 1\text{--}11 \text{ ng g}^{-1}$) are very similar to the range of total PCBs ($\sim 1.0\text{--}28 \text{ ng g}^{-1}$) measured in surface sediments off the coast of Croatia in 1977-78 (see Fowler, 1990 for review). It thus appears that there has been little, if any, decrease in PCB loading in Adriatic sediments over the past 15 years. This conclusion is further supported by other measurements obtained in 1990 from the Middle Adriatic which show PCB levels (as Aroclor 1254) ranging from 0.8 to 6.6 ng g^{-1} in surface sediments along transects between Split, Croatia and Pescara, Italy (Dujmov *et al.*, 1993). Two of the locations sampled by Dujmov *et al.* (1993) are very close to Sts. 1, 18 and 43 in the Central Jabuka Pit area (Fig. 2.). In this case the concentrations reported for 1990 (4.2 and 4.3 ng g^{-1}) were roughly a factor of four higher than the average level ($\times = 1.1$, range $0.91\text{--}1.4 \text{ ng g}^{-1}$) we measured in 1993. Nevertheless, observed differences of this order, while real, may result from small-scale spatial inhomogeneity rather than input variations or degradation over time. On the other hand, the 1990 transect data of Dujmov *et al.* (1993) do suggest a decreasing trend in PCB concentration from the open Middle Adriatic towards the Croatian coast. This is consistent with the hypothesis that anthropogenic inputs to the Adriatic are closely linked to the highly industrialised areas in the region and the influence of the westerly drift of the Po river outfall (Fowler, 1987). In comparison with other areas, the concentrations of the Aroclor 1254 and 1260 mixtures we observed in surface sediments fall well within the range of values that have been reported for nearshore and coastal sediments from the Mediterranean basin and elsewhere (Fowler, 1987, 1990).

The PCB congeners in Table 1 are, to our knowledge, the first such data reported for the Adriatic Sea. Close examination of the congener patterns shows some subtle differences among sediments which most certainly reflect inputs of different PCB compounds to each location. However, some strong trends in the data are clear. For example, PCB Nos. 138 and 153 consistently show the highest concentrations in all of the sediments examined. Furthermore, the concentrations of these two congeners are nearly the same. Concentrations of Congener Nos. 52 and 101 are also relatively high in the sediments but are consistently lower than either PCB 138 or 153. This was not the case observed in sedimenting particulate matter from the northwestern Mediterranean (Fowler *et al.*, 1990) in which PCBs 52 and 101 were most often the dominant congeners. This evidence for congener fractionation is also most likely related to variable inputs of PCB mixtures to the Mediterranean basin.

The sediment core taken in 1994 at St. 33 just south of the Po river outflow has been analysed for excess ^{210}Pb in horizons down to 32 cm. Details of the ^{210}Pb profiles in the core are reported elsewhere (Hamilton *et al.*, this volume). Interpretation of ^{210}Pb profiles in sediments which may be subject to mixing processes is difficult at best; nevertheless, assuming minimal mixing in these sediments, a minimum sedimentation rate can be estimated. Briefly, based on the slope of the exponential plot of excess ^{210}Pb against cumulative dry mass, a mass accumulation rate (r) of $0.2 \text{ g cm}^{-2} \text{ y}^{-1}$ was derived (*ibid.*). Using measured porosities for each sediment horizon in the core, an average porosity (ϕ) of 0.695 was computed for the top 20 cm of the core. Applying these values to the expression $S = r / (\rho(1 - \phi))$ results in a sedimentation rate (S) of 0.26 cm y^{-1} . If the mean PCB concentration of the two PCB mixtures in surface sediments (9.3 ng g^{-1}) is used with this sedimentation rate, an average PCB sedimentation rate of $19 \mu\text{g m}^{-2} \text{ y}^{-1}$ is computed. This value lies between corresponding rates reported for the nearshore ($29 \mu\text{g m}^{-2} \text{ y}^{-1}$) and offshore ($13 \mu\text{g m}^{-2} \text{ y}^{-1}$) areas of the northwestern Mediterranean outside the influence of rivers (Burns and Villeneuve, 1983, 1987).

Fig. 3 shows the downcore profiles of PCBs in sediments from St. 33. Because PCB concentration can be a function of lipid content (Addison, 1982), concentrations in sediments have been normalised to hexane extractable organic matter (H.E.O.M.) for facilitating comparisons with depth. Both the profiles of the two commercial mixtures as well as those for two heavily chlorinated (7 chlorine atoms) congeners (Nos. 170 and 183) show maximum values deposited between roughly 20-27 years earlier. This would correspond closely to the period of maximum PCB sales which occurred during 1969-70. Furthermore, PCBs have been produced commercially since 1929. Our data, particularly those for the heavily-chlorinated, non-degradable PCB congeners, show rapid drop-off in PCBs by the 18-20 cm horizons which corresponds closely to the period when one would expect to see the compounds first entering the environment. Both of these features evident in the PCB profiles support the ^{210}Pb -derived sedimentation rate of approximately 0.3 cm y^{-1} we computed. The high stability of this group of organic compounds coupled with their known production history make them excellent markers for comparing with independently-derived sedimentation rates.

The high resolution profile of PCB compounds can also be used to calculate a total inventory of sedimented PCBs in this region. Using a dry sediment density of 2.56 g cm^{-3} , a summation of PCBs in the different depth intervals through 18 cm gives total inventories of 0.44 and 0.37 kg km^{-2} of PCB quantified as Aroclor 1254 and 1260, respectively. These amounts are very similar to an inventory of 0.41 kg km^{-2} (as Aroclor 1254) that can be computed for nearshore sediments sampled in 1981 from the northwestern Mediterranean (Burns and Villeneuve, 1983), but are higher than an average value of 0.17 kg km^{-2} for western Mediterranean sediments derived from Burns and Villeneuve (1987). The observed difference is most likely due to the higher sedimentation rates and PCB inputs in nearshore regions like the Po river outflow.

Mercury. Total Hg concentrations in the same sediment samples are set out in Table 2. As with PCBs, the total mercury concentrations in the surface sediment layer closely reflect proximity to anthropogenic inputs. The two sampling sites under the influence of the Po (Sts. 113 and 165) contained Hg concentrations of 403 and 499 ng g^{-1} , respectively. In contrast, total concentrations in sediments from the Jabuka Pit in the open Middle Adriatic were low ranging from 67 - 224 ng g^{-1} .

A recent study of sediment grab samples from throughout the Adriatic Sea concluded that mercury concentrations in sediments decreased from the northern to the southern sectors (Ferrara and Maserti, 1992). In the Northern Adriatic, Ferrara and Maserti (1992) reported values ranging from 50 to 8630 ng g^{-1} dry, with the maximum values found offshore from the mouth of the Isonzo river (8630 ng g^{-1}) and the Marano lagoon (7220 ng g^{-1}). These latter values were an order of magnitude higher than concentrations found at the other sites and likely reflected inputs from mercury mines in the Isonzo river basin and a chloralkali plant located near the Marano lagoon. It is clear from their surface sediment values that Hg concentrations were significantly higher in the northern sector. Total Hg values at five stations sampled by those authors in 1990 offshore from the Po river mouth averaged 420 ng g^{-1} dry (range 250 - 730 ng g^{-1}). Concentrations we measured in 1993 at five stations in the same general area ($\bar{x} = 338$, range 168 - 499 ng g^{-1}) were quite similar. In contrast, Ferrara and Maserti (1992) reported a Hg concentration of 40 ng g^{-1} dry in a single sediment sample in the Jabuka Pit which was lower than the three values we measured in sediments from Sts. 1, 18 and 43 in the same area (range 67 - 224 ng g^{-1} , Table 2). While we are unaware of other mercury data from the open Middle Adriatic, it can be concluded from our measurements and those of Ferrara and Maserti (1992) that mercury levels in sediments are substantially lower than concentrations in the Northern Adriatic which is under the influence of both anthropogenic and relatively high natural inputs of mercury. Furthermore, such concentrations as have been measured in the Middle Adriatic are of the same order as those which have been reported in other offshore areas of the Mediterranean Sea (Bargaglia *et al.*, 1988; Fowler, 1990).

It is also instructive to examine metal profiles in sediments to obtain insights into the historical record of contaminant inputs and fluxes to bottom sediments. In a dated core located just south of the Po outflow (St. 33), Hg concentrations were examined to a depth of 32 cm . Levels at all depths were relatively high decreasing gradually from approximately 400 ng g^{-1} in the top 4 cm to roughly 200 ng g^{-1} at depth (Fig. 4). The same but stronger trend is noted for methyl Hg which decreased from

a maximum of 650 $\mu\text{g g}^{-1}$ in the surface layer of the core to approximately 150 $\mu\text{g g}^{-1}$ at 30 cm depth (Fig. 4). Mean grain size of the sediment was relatively constant with depth and, therefore, is not considered a major factor which would greatly affect the mercury concentrations. On the other hand mercury, particularly methyl mercury, is closely associated with organic matter and therefore is often a function of the organic carbon content. For this reason mercury concentrations were normalised to POC in the sediment and the resultant profiles are shown in Fig. 5. The profiles are complex and difficult to interpret; however, no real depth trend is evident for total Hg, whereas the normalised methyl Hg profile appears to show two maxima, one at 10 cm and the other at 22 cm depth. We are unaware of any other published information on methyl Hg in the Adriatic. It is noteworthy that both total and methyl Hg peak in the 20-22 cm depth horizon which corresponds to an approximate time interval of 77-85 years before the core was raised. The observed maxima may therefore be related to the year of maximum Hg production (i.e. 1913) when the Idria mine on the Isonzo river produced twice the average amounts of Hg in all other years before or after that date (M. Horvat, unpublished results).

The only other comparable data on Hg in cores are those from coastal sediments (<20 m water depth) sampled just outside the Venice lagoon (Donazzolo *et al.*, 1984). In three separate cores, Donazzolo *et al.* (1984) reported values ranging from around 200 ng g^{-1} dry in the surface to less than 100 ng g^{-1} at depth. Two showed enrichment ($\sim 200 \text{ ng g}^{-1}$) in the surface layer and the third displayed low Hg concentrations in the surface and a Hg maximum ($\sim 150 \text{ ng g}^{-1}$) in the deepest layer ($\sim 50 \text{ cm}$). In two of the cores the highest Hg concentrations were associated with sand rather than the pelite ($<63 \mu\text{m}$) fraction. Unfortunately, the resolution of their profiles is not high and, therefore, it is difficult to establish any clear trends.

Using a ^{210}Pb -derived mass sedimentation rate of $0.2 \text{ g cm}^{-2} \text{ y}^{-1}$, we can compute the recent Hg sedimentation rate at St. 33 off the Po delta. The values obtained are approximately 0.75 $\text{mg total Hg m}^{-2} \text{ y}^{-1}$ and 1.1 $\mu\text{g methyl Hg m}^{-2} \text{ y}^{-1}$.

Trace elements. Several other trace elements were analysed in the surface sediments which were collected for radionuclides, carbon, mercury and PCB analyses. The results for the ICP-MS runs are set out in Table 3. Ni, Cr, Co, Pb and Zn, all elements whose levels can be affected by anthropogenic inputs, show relatively low concentrations which do not suggest major contamination in these areas. The concentrations of these five heavy metals all generally fall within the range of values that have been reported for specific areas in the Northern Adriatic (e.g., see Donazzolo *et al.*, 1984; Faganeli *et al.*, 1991).

Although the data are far from comprehensive, some north-south trends related to the sources of known contaminant input are evident. For example, Pb concentrations in the Northern Adriatic ($x = 44$, range 25-68 $\mu\text{g g}^{-1}$) are on average twice as high as those found in the Middle Adriatic ($x = 22$, range 18-27 $\mu\text{g g}^{-1}$). Likewise, average Zn levels in the Northern Adriatic ($x = 126$, range 69-202) are nearly double concentrations measured in sediments from the more open waters of the Middle Adriatic (Table 3). On the other hand, neither Cr, Ni nor Co showed any north-south trend in concentration. In contrast, the highest concentrations of Mn and in one case Ni were found in sediments from the Jabuka Pit (St. 1 and 18); these levels may in fact be related to enhanced deposition of Mn oxides in this deeper region. Arsenic levels were also considerably higher in two of the three Jabuka Pit cores and, therefore, would most likely be related to the particular geochemistry of these sediments rather than to anthropogenic inputs. No other data on As in Adriatic sediments have come to our attention; however, the maximum levels found (85-90 $\mu\text{g g}^{-1}$ dry) are roughly three to four times higher than concentrations reported for nearshore sediments from the Persian Gulf (Fowler *et al.*, 1993).

4. Summary and conclusions

The 1993-94 synoptic survey of selected organochlorine compounds, mercury and other trace elements in Adriatic sediments was very useful in establishing recent trends in both spatial and temporal distributions of these potential pollutants. The data show that, in general, there is a trend towards higher concentrations of trace contaminants in the Northern Adriatic sediments than in corresponding sediments from the Middle Adriatic. This is most certainly related to the greater industrial and

domestic activities surrounding the relatively shallow northern sector, and particularly to inputs of anthropogenic substances via the Po river whose drainage basin includes much of the highly industrialised region of Northern Italy. In the case of anthropogenically-derived mercury, the same input sources are considered to contribute to mercury loading of modern day sediments; however, the proximity of the Northern Adriatic basin to the mercury anomaly and mines in the Isonzo river basin has had a marked effect on mercury distributions in Northern Adriatic sediments. Not only may the anomaly have led to a generally higher mercury background in Northern Adriatic sediments, but pulses in mercury production and presumed inputs are evident from historical records in sediments. Analysis of sediment cores from the central basin (e.g., Jabuka Pit) would furnish further insight into the extent to which mercury entering from the Isonzo river has distributed southward over the last century.

As concerns the existing levels of PCBs in the Adriatic, our observations confirm little reduction in PCB loading of the ecosystem over the past two decades despite significant reduction in their usage during that time. This fact attests to the persistence of these toxic compounds in the marine environment. In terms of absolute concentrations, the existing levels of PCB in Adriatic sediments are similar to and in some cases lower than those which have been measured previously in nearshore and coastal sediments from other areas of the Mediterranean Sea and elsewhere. In the case of total mercury, very high concentrations are known to exist in sediments off the mouth of the Isonzo river. Despite such high inputs, substantial loading appears to be present only very near the source term. This is translated to much lower levels in surface sediments throughout the Northern Adriatic basin and especially in the Middle Adriatic. In spite of such substantial inputs of natural mercury in the region, the concentrations measured in sediments are very similar to levels measured in the the Mediterranean basin and other oceanic regions. Hence, the only area which may be impacted by mercury contamination is the sector very near to the obvious source terms in the Northern Gulf of Trieste. On the other hand, distribution data for Pb and Zn obtained during the ELNA project and from previous studies suggest that the Po river is a primary input source for these metals in the Adriatic.

The extent to which trace contaminant loading in the Northern Adriatic is closely linked to the eutrophic situation there is still far from clear. Although several studies have demonstrated a relationship between PCB compounds and mercury and organic carbon content of particles and sediments, the relatively high carbon burial rates which have occurred in some areas of the Northern Adriatic basin (e.g., $0.21-1.15 \text{ m Mol cm}^{-2} \text{ y}^{-1}$ (Hamilton *et al.*, this volume) have not led to unusually high trace contaminant concentrations in the same sediments analyzed in this study. However, to more carefully examine this relationship, additional cores are needed in which both organic carbon and trace contaminant levels are well-documented. Comparison of such cores with those from outside the Adriatic should furnish additional insight into the processes governing sequestration and removal of both carbon and anthropogenic contaminants to the sediments.

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Table 1 Concentrations of PCB congeners (ng g⁻¹ dry) in surface sediments from different regions of the Adriatic collected in 1993
(See Fig. 2 for station locations)

<i>PCB Compounds/ Congeners</i>	<i>Middle</i>			<i>North-Middle</i>		<i>Northern</i>		
	<i>Station 1</i>	<i>Station 18</i>	<i>Station 43</i>	<i>Station 82</i>	<i>Station 113</i>	<i>Station 126</i>	<i>Station 154</i>	<i>Station 165</i>
Dry wt./Wet wt.	0.292	0.373	0.268	0.475	0.339	0.575	0.377	0.379
*HEOM (mg g ⁻¹)	0.03	0.04	0.05	0.07	0.22	0.07	0.14	0.22
Aroclor 1254	0.91	1.4	0.91	3.2	4.8	1.6	2.7	7
Aroclor 1260	1.5	1.5	2.3	3.5	11	3.8	7.2	10
PCB 8	0.1	0.01	0.01	0.16	0.13	0.05	0.11	0.1
PCB 18	0.14	0.03	0.03	0.15	0.11	0.05	0.12	0.12
PCB 28	0.2	0.04	0.04	0.29	0.26	0.09	0.21	0.38
PCB 31	0.2	0.04	0.05	0.24	0.17	0.07	0.16	0.29
PCB 44	0.12	0.03	0.13	0.2	0.13	0.05	0.13	0.31
PCB 49	0.1	0.06	0.05	0.27	0.2	0.11	0.15	0.71
PCB 52	0.21	0.16	0.13	0.3	0.37	0.19	0.33	0.75
PCB 66/95	0.08	0.18	0.13	0.25	0.44	0.16	0.28	1
PCB 87	0.06	0.08	0.06	0.16	0.19	0.1	0.13	0.27
PCB 97	0.01	0.03	0.02	0.06	0.08	0.04	0.06	0.19
PCB 101	0.12	0.23	0.12	0.46	0.75	0.37	0.44	1.1
PCB 105	0.07	0.1	0.07	0.22	0.39	0.16	0.25	0.52
PCB 110/77	0.13	0.16	0.09	0.57	0.66	0.25	0.41	1
PCB 118	0.14	0.1	0.1	0.45	0.81	0.33	0.58	1.3
PCB 128	0.08	0.06	0.09	0.1	0.31	0.12	0.2	0.45
PCB 138	0.25	0.23	0.28	0.85	1.9	0.73	1.3	2.1
PCB 149	0.18	0.13	0.13	0.54	0.9	0.37	0.6	0.96
PCB 153	0.24	0.24	0.3	0.85	2	0.75	1.3	2.1
PCB 170	0.06	0.11	0.08	0.15	0.61	0.21	0.41	0.67
PCB 174	0.04	0.04	0.07	0.15	0.39	0.13	0.23	0.38
PCB 177	0.02	0.02	0.02	0.12	0.29	0.1	0.19	0.25
PCB 180	0.15	0.14	0.17	0.35	1.1	0.37	0.72	1.2
PCB 183	0.03	0.04	0.05	0.09	0.23	0.08	0.15	0.22
PCB 187	0.1	0.06	0.07	0.34	0.81	0.29	0.57	0.78
PCB 194	0.03	0.05	0.05	0.07	0.23	0.07	0.15	0.27
PCB 200	N.D.	0.01	0.01	0.03	0.06	0.03	0.05	0.11

* HEOM = Hexane extractable organic matter N.D.: Not detected

Table 2 Total Hg concentration in surface sediments from different regions of the Adriatic Sea, 1993

<i>Station</i>	<i>Region</i>	<i>Replicat 1</i> (ng/g)	<i>Replicat 2</i> (ng/g)	<i>MEAN</i> (ng/g)	<i>STD</i> (ng/g)	<i>RSD</i> (%)
113	Northern	388	419	403	22.0	5.5
126		162	173	168	7.2	4.3
154		248		248		
165		499		499		
82	North-Middle	189		189		
1	Middle	224		224		
18		67		67		
43		86		86		

Table 3 Trace element concentrations ($\mu\text{g g}^{-1}$ dry) in surface sediments from different regions of the Adriatic Sea (See Fig. 2 for station locations)

<i>Region</i>	<i>Sample</i>	<i>Li</i>	<i>Mn</i>	<i>Co</i>	<i>Ni</i>	<i>Cr</i>	<i>Zn</i>	<i>As</i>	<i>Ba</i>	<i>Pb</i>	<i>Th</i>	<i>U</i>
<i>$\mu\text{g g}^{-1}$ (dry wt.)</i>												
Northern	ELNA 2 - St. 61	39	488	9	46	28	120	17	244	44	7.7	2.3
"	ELNA 3 - St. 126	31	694	13	48	9	69	11	220	25	6.8	1.7
"	ELNA 7 - St. 41	105	1450	39	138	46	202	37	496	68	17.7	5.0
"	ELNA 6 - St. 66	52	1190	15	69	21	111	17	197	39	7.6	2.0
North-Middle	ELNA 3 - St. 82	55	972	13	112	17	74	90	280	27	-	2.1
Middle	ELNA 6 - St. 103	30	769	14	70	15	65	17	162	18	5.2	1.5
"	ELNA 3 - St. 01	33	2231	14	67	20	51	19	165	22	6.7	1.5
"	ELNA 6 - St. 87	53	972	13	112	17	74	90	284	27	-	2.1
"	ELNA 3 - St. 18	51	2722	27	194	32	105	85	217	23	7.2	1.7

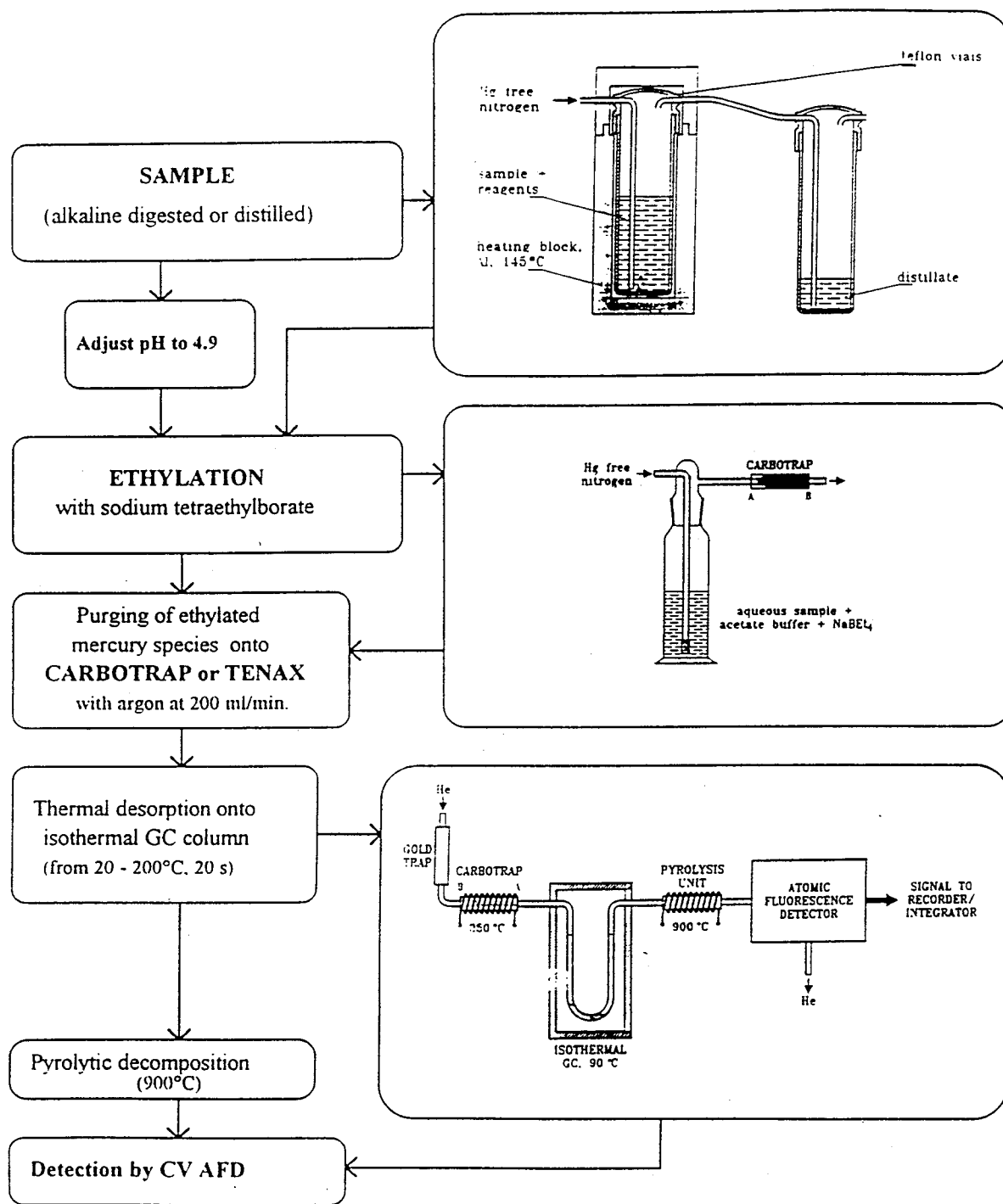


Fig. 1. Schematic diagram of the analytical method for measuring methyl mercury in sediments.

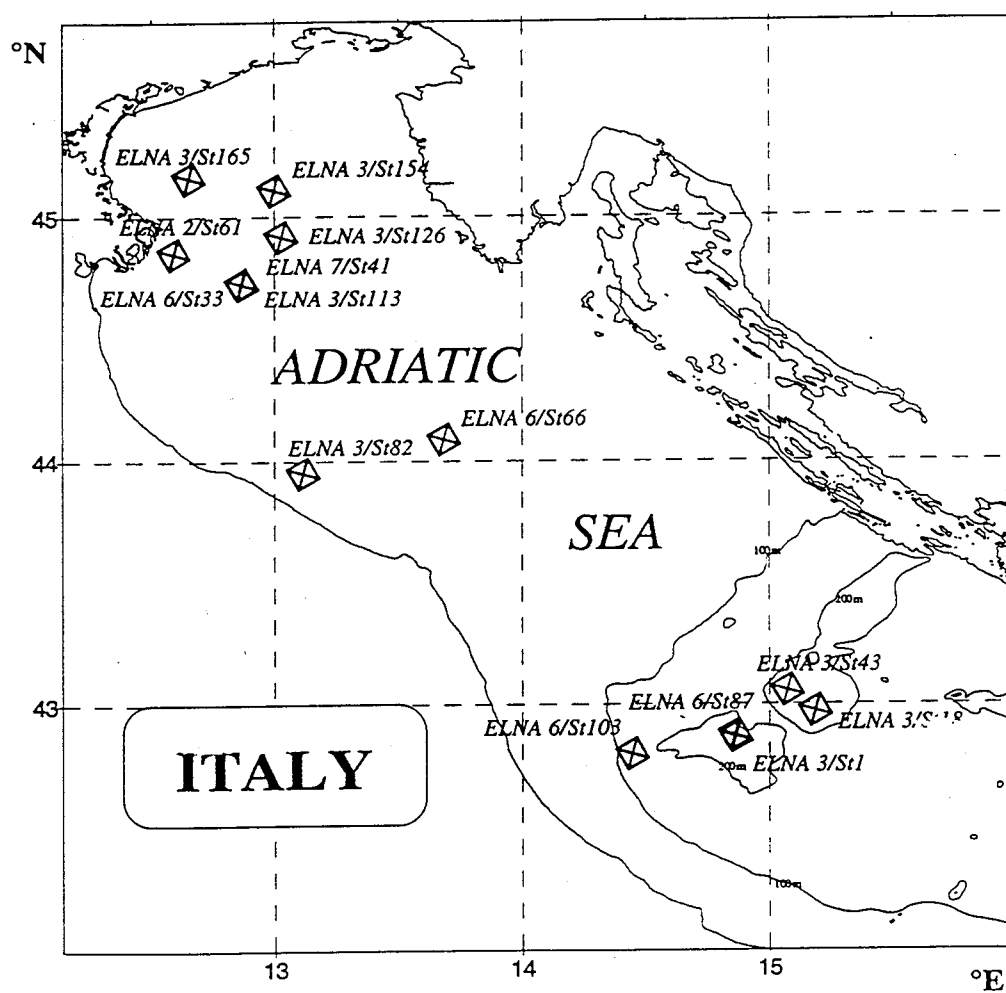


Fig. 2 Location of sediments analysed for trace contaminants.

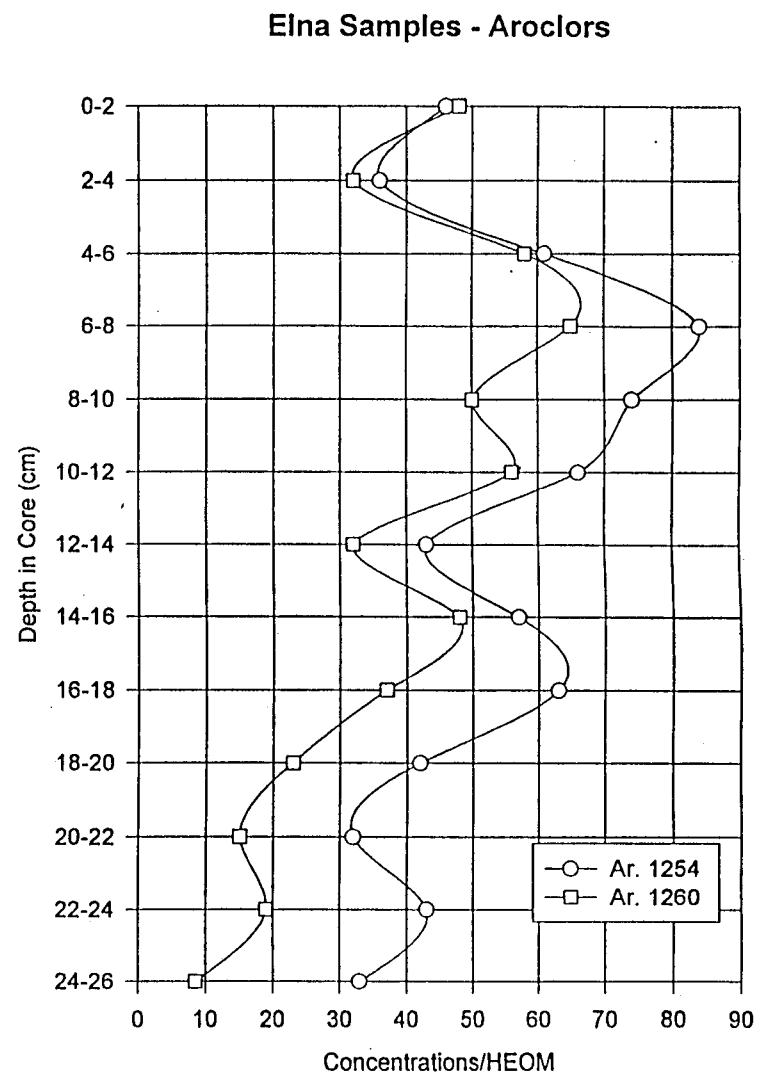
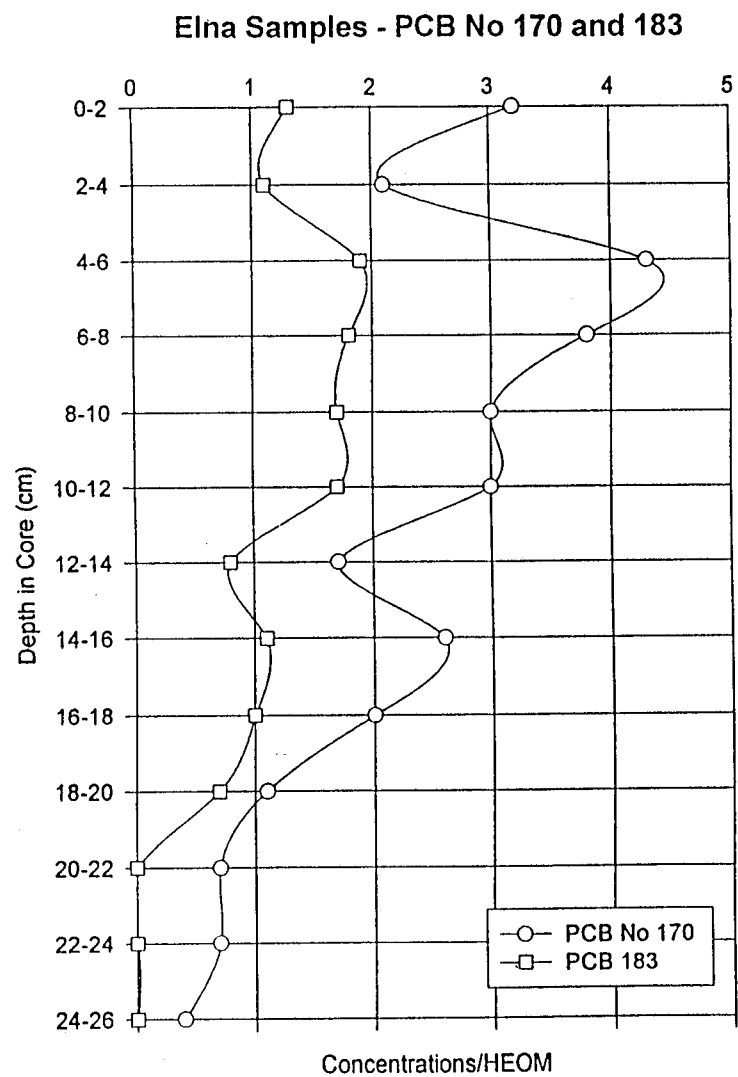


Fig. 3 PCB mixtures and congeners in a sediment core collected at St. 33 near the outflow of the Po river during 1994. PCB concentrations have been normalised to H.E.O.M.

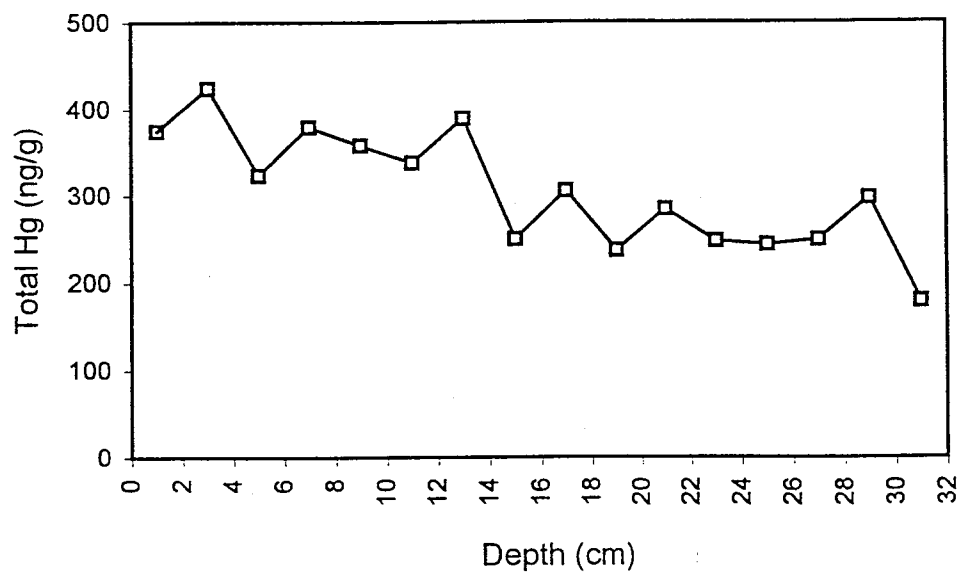
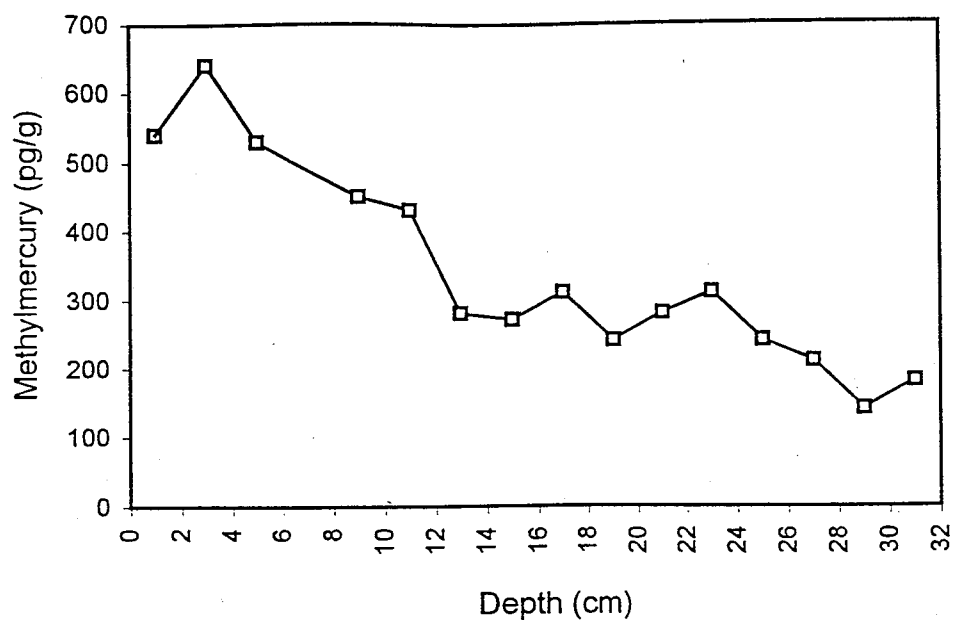


Fig. 4 Downcore profiles of total Hg and methyl Hg concentrations in sediments collected from St. 33 near the outflow of the Po river during 1994

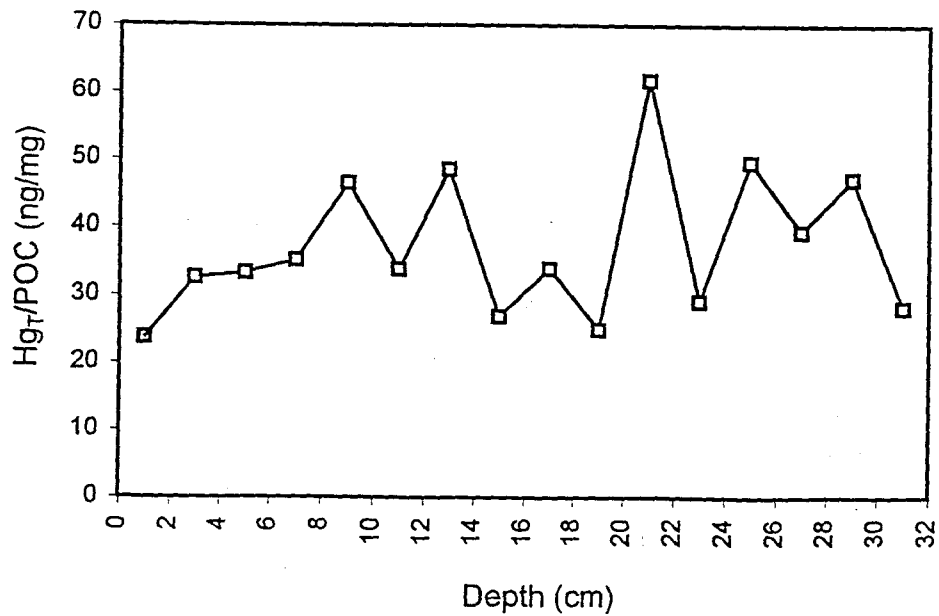
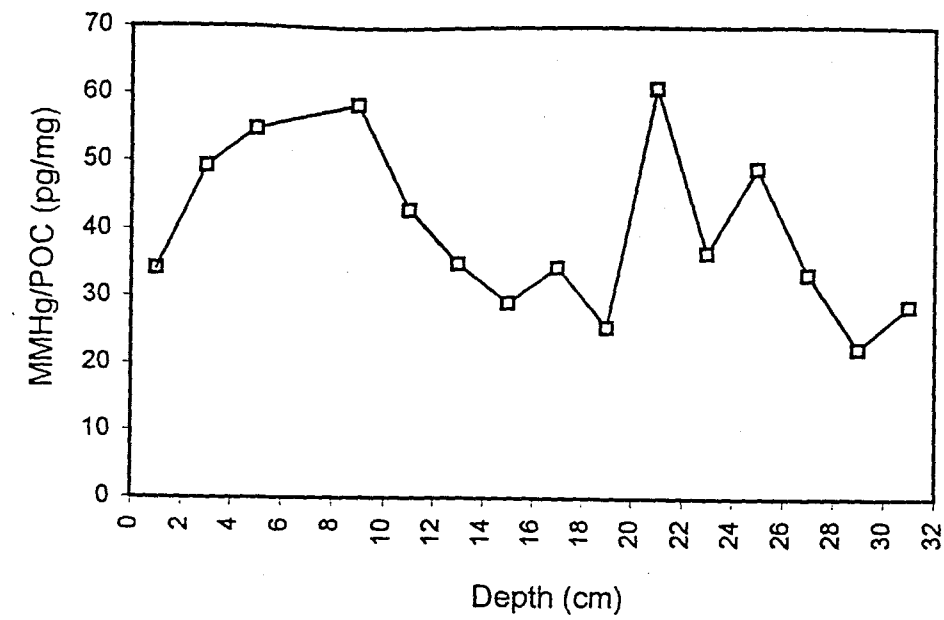


Fig. 5 Downcore profiles of total Hg and methyl Hg concentrations normalised to POC in sediments collected from St. 33 near the outflow of the Po river during 1994

University of California
Lawrence Livermore National Laboratory
Technical Information Department
Livermore, CA 94551

